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(54) ROOM-TEMPERATURE-CURABLE COMPOSITION

(57)Abstract:

PURPOSE: To obtain a room-temp.-curable compsn. which exhibits a sufficient depth cure rate and is free from troubles, such as the viscosity increase of the main component, even during long stroage by compounding a specific org. polymer with a cure catalyst, an org. amine compd., and a filler.

CONSTITUTION: This compsn. is prepd. by mixing and kneading 100 pts.wt. org. polymer which is derived from a hydroxylated polyoxyalkylene polymer obtd. by polymerizing an alkylene oxide using an initiator in the presence of a composite metal cyanide complex as the catalyst and has hydrolyzable silicon groups represented the formula (R1 is a 1-20C monovalent hydrocarbon group, R2 is a divalent org. group; X is a hydroxyl or hydrolyzable group; and a is 1-3) and a total content of ionic impurities of 50ppm or lower with 0.01-10 pts.wt. cure catalyst selected from among 20C or lower aliph. carboxylates of divalent tin, divalent bismuth, and divalent lead, 0.01-10 pts.wt. org. amine compd., 50-250wt.% (based on the polymer) filler, and optional plasticizers and additives.



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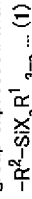
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CLAIMS

[Claim(s)]

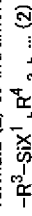
[Claim 1] A curing catalyst (B) chosen from the following organic polymer (A), carboxylate of divalent tin, carboxylate of divalent bismuth, and carboxylate of divalent lead, and an organic amine compound (C) and a room-temperature-curing nature constituent containing a bulking agent (D). (Organic polymer) It is derived from a hydroxyl group content polyoxyalkylene polymer (F) produced by polymerizing alkylene oxide in an initiator by making a composite metal cyanide complex (E) into a catalyst. An organic polymer (A) whose total amount of an ionic impurity it has a hydrolytic silicon group expressed with a formula (1), and is 50 ppm or less.



As for R^1 , a hydroxyl group or a hydrolytic basis, and a of substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and R^2 are the integers of 1-3 a divalent organic group and X among a formula.

[Claim 2] A room-temperature-curing nature constituent of Claim 1 whose organic amine compound (C) is with a carbon number of 20 or less amine.

[Claim 3] Claim 1 or 2 room-temperature-curing nature constituents which are a compound in which an organic amine compound (C) has a hydrolytic silicon group expressed with an amino group and a formula (2) to intramolecular.

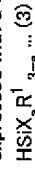


As for a divalent organic group and R^4 , a hydroxyl group or a hydrolytic basis, and b of substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and X^1 are [R^3] the integers of 1-3 among a formula.

[Claim 4] A room-temperature-curing nature constituent of either of the Claims 1-3 which is an ionic impurity in which an ionic impurity contains metallic compounds and/or an alkali metal compound resulting from a composite metal cyanide complex (E).

[Claim 5] An organic polymer (A) an ionic impurity contained in a polymer (F). After an ionic impurity contained in a polymer (F) by removing this salt from a polymer (F) after considering it to a polymer (F) as an insoluble salt intrinsically shall be 50 ppm or less. A room-temperature-curing nature constituent of either of the Claims 1-4 which is an organic polymer produced by introducing a hydrolytic silicon group into a polymer (F).

[Claim 6] An organic polymer (A) an ionic impurity contained in a terminal unsaturated group introduction thing (G) of a polymer (F). After an ionic impurity contained in a terminal unsaturated group introduction thing (G) by removing this salt from a terminal unsaturated group introduction thing (G) after considering it in a terminal unsaturated group introduction thing (G) as an insoluble salt intrinsically shall be 50 ppm or less. A room-temperature-curing nature constituent of either of the Claims 1-4 which is an organic polymer obtained by making it react to a silicon hydride compound expressed with a terminal unsaturated group introduction thing (G) and a formula (3).



A hydroxyl group or a hydrolytic basis, and a of R^1 are the integers of 1-3 among a formula substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and X.

[Claim 7] A room-temperature-curing nature constituent of either of the Claims 1-6 whose hydroxyl

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value conversion molecular weights of a polymer (F) are 5000-30000.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

- [0001] [Industrial Application] This invention relates to the room-temperature-curing nature constituent hardened under hygroscopic-surface-moisture existence.
- [0002] [Description of the Prior Art] The method of using it for a sealing material, adhesives, etc., using the hardening reaction of various kinds of organic polymers which have a hydrolytic silicon group at the end which is known as conventional, for example, modified silicone, system resin is known well, and is a useful method industrially.
- [0003] [Problem(s) to be Solved by the Invention] The organic polymer which has a hydrolytic silicon group at such the end is proposed by JP,45-36319,B, JP,46-17553,B, JP,61-18582,B, etc., for example.
- [0004] In order to give room-temperature-curing nature to an end especially with the organic polymer which has alkoxy silyl groups as a hydrolytic silicon group among the organic polymers which have a hydrolytic silicon group, using what is called a curing catalyst is usually performed. As such a curing catalyst, organic metallic compounds, such as metal salt of carboxylic acid, acidity, or a basic compound is known, and carboxylate of tin and other organotin compounds are especially common.
- [0005] To the organic polymer which has a hydrolytic silicon group at the end, various bulking agents, a plasticizer, it is divided roughly into 2 gestalten called what is called a 1 liquid type and a 2 liquid type as a gestalt of the combination when using the resin composition of the room-temperature-curing nature which blends an adhesive grant agent, a thixotropy grant agent, a curing catalyst, various stabilizer, etc. for a sealing material, adhesives, etc.
- [0006] What is known as a 2 liquid type among those is divided into base resin and a hardening agent, it mixes colorant etc. with these two ingredients if needed further, constructs, and makes it harden in a service space at the time of use. As for the hardening agent in this 2 liquid type, it is common to include the curing catalyst, and as this curing catalyst, since a hardened material shows good compression restoration nature to a repetition of elasticity, leaden carboxylate or carboxylate of divalent tin and the organic amine compound, and the method of specifically using octylic acid tin and lauryl amine are proposed (refer to JP,61-60867,B).
- [0007] However, in a 2 liquid type, as an organic polymer which has an end hydrolytic silicon group, . . . Were manufactured by the method of introducing a hydrolytic silicon group, after a dihalo compound's tying the polyether compound of the comparatively short molecular weight proposed by the aforementioned well-known example, setting it and carrying out Polymer Division quantification. If octylic acid tin and lauryl amine are used as a curing catalyst when the polymer and bulking agent which have a hydrolytic silicon group are used as base resin, by a part far from the surface of a cure rate, especially a cured body, the so-called cure rate of the depths is insufficient, and it cannot be satisfied.
- [0008] When the organic polymer containing the hydrolytic silicon group manufactured by the end from the polyoxyalkylene polymer which manufactured as a catalyst the composite metal cyanide complex given [as an organic polymer which has a hydrolytic silicon group] in JP,3-43449,A and JP,3-79627,A is used as base resin, in order not to usually perform strict moisture control (that is, let the amount of [in base resin] water content fall) when manufacturing base resin although the hardenability of the depths improves remarkably if this curing catalyst is used, there was a case

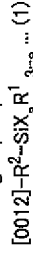
where the viscosity of base resin rose during long-term preservation, and use top inconvenience arose.

[0009]

[Means for Solving the Problem] This invention is the following invention which is going to cancel such a fault.

[0010] A curing catalyst (B) chosen from the following organic polymer (A), carboxylate of divalent tin, carboxylate of divalent bismuth, and carboxylate of divalent lead, and an organic amine compound (C) and a room-temperature-curing nature constituent containing a bulking agent (D).

[0011] (Organic polymer) It is derived from a hydroxyl group content polyoxyalkylene polymer (F) produced by polymerizing alkylene oxide in an initiator by making a composite metal cyanide complex (E) into a catalyst. An organic polymer (A) whose total amount of an ionic impurity it has a hydrolytic silicon group expressed with a formula (1), and is 50 ppm or less.



[0013] As for R^1 , a hydroxyl group or a hydrolytic basis, and a of substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and R^2 are the integers of 1-3 a divalent organic group and X among a formula.

[0014] (Organic polymer) An organic polymer (A) is derived from a hydroxyl group content polyoxyalkylene polymer (F) produced by polymerizing alkylene oxide in an initiator by making a composite metal cyanide complex (E) into a catalyst.

[0015] By using a composite metal cyanide complex (E), using the conventional alkaline metal catalyst, M_w/M_n is [rather than] small and a hydroxyl group content polyoxyalkylene polymer (F) of hydroviscosity can be obtained more in the amount of Polymer Division.

[0016] A complex which uses zinc hexa cyanocobaltate as the main ingredients as a composite metal cyanide complex (E) is preferred, and the ether and/or especially an alcoholic complex are preferred. The presentation can use what is intrinsically indicated to JP,546-27250,B. As ether, ethyleneglycol dimethyl ether (glyme), diethylene glycol dimethyl ether (jig lime), etc. are preferred, and especially glyme is preferred from handling at the time of manufacture of a complex. As alcohol, t-butanol is preferred.

[0017] A compound which has 2-10 active hydrogen as an initiator is preferred, a polyhydroxy compound is preferred, and a polyhydroxy compound which has 2-4 hydroxyl groups especially is preferred 2-8 pieces. Specifically Ethylene glycol, a diethylene glycol, propylene glycol, Dipropylene glycol, neopentyl glycol, 1,4-butanediol, There is polyol of low molecular weight from an object produced by making alkylene oxide react to 1,6-hexanediol, glycerin, trimethylolpropane, pentaerythritol, diglycerol, a shock sirloin, and these. One-sort single use or two or more sorts of concomitant use may be sufficient as these. An unsaturation group content mono- hydroxy compound like allyl alcohol can also be used.

[0018] A total amount of an ionic impurity of an organic polymer (A) of this invention is 50 ppm or less. This invention is suitable when especially an ionic impurity is an ionic impurity containing metallic compounds and/or an alkali metal compound resulting from a composite metal cyanide complex (E). It is preferred that ionic impurities are 30 ppm or less and 20 more ppm or less.

[0019] By reducing such metal impurity quantity, the storage stability of an organic polymer (A) and a hardenability constituent of this invention is improved more, and also hardenability which was excellent in order not to bar an operation of a curing catalyst is acquired.

[0020] Following (I) - a method of (III) are mentioned as the reducing method. Methods of using it, when removing metallic compounds resulting from especially a composite metal cyanide complex (E) include (III). (I) Especially since a method can reduce an ionic impurity effectively and economically, it is desirable.

[0021] (I) How to remove this salt from a polymer after making into an insoluble salt intrinsically an ionic impurity contained in a polymer to a polymer. After adding the Nonion system surface-active agent [a compound, water, and if needed] which specifically react to an ionic impurity and can form an insoluble salt to a polymer intrinsically, by drying, a salt is deposited and there is a method of next removing this salt. As a compound which can form a salt, chloride, sulfuric acid, nitric acid, phosphoric acid, pyrophosphoric acid, disodium dihydrogen pyrophosphate, etc. are preferred. A deposited salt is removable by filtration operation, adsorbing operation, etc.

[0022](II) How to make an anion exchange resin and/or cation exchange resin contact, and to remove an ionic impurity after adding a solvent to a polymer.

[0023]To a buffer for pH and arbitration, by ammonia and a chelating agent (III) After processing, A method of removing metallic compounds which originate in a composite metal cyanide complex (E) after adding a method and fatty alcohol from which metallic compounds resulting from a composite metal cyanide complex (E) are removed, and a chelating agent, a method of removing metallic compounds which originate in a composite metal cyanide complex (E) after processing with an oxidizer.

[0024] With an ionic impurity as used in the field of this invention, originate in a composite metal cyanide complex (E). A cation and anions, such as zinc ion, cobalt ion, cyanide ion, and a chloride ion; Mix as an impurity at a process of manufacturing an organic polymer (A). Sodium ion, alkali metal ion like potassium ion, carboxylate ion that polyoxyalkylene generated in response to oxidation at a process of manufacturing a halogen ion; organicity polymer (A); An organic polymer (A) at a process to manufacture An ester bond. All the anions, such as catalyst metal salt added when making carbonate combination etc. form, and cations are included.

[0025]As for an organic polymer (A), what replaced a hydrogen atom in a hydroxyl group of a hydroxyl group content polyoxyalkylene polymer (F) by a formula (1) is preferred.

[0026]As for the number of hydroxyl groups per molecule of a polyoxyalkylene polymer (F) used for this invention, it is preferred that they are 2-10 pieces. It is especially preferred from balance of physical properties, such as viscosity, intensity, and elongation, that they are especially 2-4 pieces 2-8 pieces.

[0027]Desirable polymers (F) are polyoxypropylene diol, polyoxypropylene triol, and polyoxypropylene tetraol. When using for a method of the following (b) or (**), unsaturation group end polyoxyalkylene monoacars, such as polyoxypropylene glycol monoallyl ether, can also be used.

[0028]As for a hydroxyl value conversion molecular weight of a polyoxyalkylene polymer (F), 5000-30000 are preferred, and 8000-30000 are more preferred.

[0029]A hydroxyl value conversion molecular weight of this invention says a thing of a molecular weight calculated by a product of a functional group number of an initiator, and a molecular weight per hydroxyl group of polyoxyalkylene of a polymer used when manufacturing a polyoxyalkylene polymer (F) containing terminal hydroxyl groups.

[0030]An organic polymer (A) has a hydrolytic silicon group expressed with a formula (1).

[0031]-R²-SiX_aR¹_{3-a} ... (1)

[0032]As for R¹, a hydroxyl group or a hydrolytic basis, and a of substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and R² are the integers of 1-3 a divalent organic group and X among a formula.

[0033]R in a formula (1) is a divalent organic group. R¹ is a univalent hydrocarbon group substitution of the carbon numbers 1-20, or unsubstituted, and are a with a carbon number of eight or less alkyl group, a phenyl group, and a fluoro alkyl group preferably. They are a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, a cyclohexyl group, a phenyl group, etc. especially preferably.

[0034]X is a hydroxyl group or a hydrolytic basis, and is a halogen atom, an alkoxy group, an acyloxy group, an amide group, an amino group, an aminoxy group, a KETOKISHI mate group, and a hydride group as a hydrolytic basis, for example. As for especially a carbon number of a hydrolytic basis which has a carbon atom among these, four or less are [six or less] preferred. As desirable X, a with a carbon number of four or less lower alkoxy group especially a methoxy group, an ethoxy basis, a propoxy group, etc. can be illustrated. a is an integer of 1-3 and 2 or 3 is preferred.

[0035]Next, a manufacturing method of an organic polymer (A) is explained. The organic polymer (A) in this invention can introduce a hydrolytic silicon group into an end of a hydroxyl group content polyoxyalkylene polymer (F) by a method which is stated to the following (**)-(**). Such a compound is liquefied at a room temperature, and when a cured body holds pliability and uses for a sealing material, adhesives, etc. also at low temperature comparatively, it is provided with the desirable characteristic.

[0036](**) A method to which a silicon hydride compound expressed with a terminal unsaturated group introduction thing (G) and a formula (3) of a polymer (F) is made to react.

[0037]HSiX_aR¹_{3-a} ... (3)

[0038]However, R¹ in formula X, and a are the same as the above.

[0039]As a method of obtaining a terminal unsaturated group introduction thing (G) of a polymer (F), After setting terminal hydroxyl groups OH of a polymer (F) to OM (M is an alkaline metal), There is a method of making a compound which has a functional group which can react to a method or an unsaturation group, and a hydroxyl group which are made to react to unsaturation group content halogenated hydrocarbon, such as an allyl chloride, react to a polymer (F), and combining by ester bond, a urethane bond, carbonate combination, etc. When polymerizing alkylene oxide in manufacture of a polymer (F). It is obtained also by using a terminal unsaturated group content mono- hydroxy compound as a method of introducing an unsaturation group into a side chain, or an initiator by carrying out copolymerization of the unsaturation group content alkylene oxide, such as allyl glycidyl ether.

[0040](**) How to make a polymer (F) react to a compound which has a hydrolytic silicon group expressed with an isocyanate group and a formula (1).

[0041](**) A method to which W basis of a silicon compound expressed with a formula (4) to this isocyanate group is made to react after making polyisocyanate compounds, such as tolylene diisocyanate, react to a polymer (F) and considering it as an isocyanate group end.

[0042]R¹_{3-a}-SiX_a-R²W ... (4)

[0043]However, R¹ in formula X, and a -- the above -- the same -- R² are a divalent organic group and the active hydrogen containing group as which W was chosen from a hydroxyl group, a carboxyl group, a sulfinyl group, and an amino group (the 1st class or the 2nd class).

[0044](**) A method to which an unsaturation group of a terminal unsaturated group introduction thing (G) of a polymer (F) and a sulfinyl group of a silicon compound expressed with a formula (4) whose W is a sulfinyl group are made to react.

[0045]As for removal of an ionic impurity, it is preferred to carry out in suitable stages before making each silicon compound react in each procedure of the above-mentioned (b) - (**), and it sets the total amount to 50 ppm or less. That is, a following method can be illustrated.

[0046]After making into an insoluble salt intrinsically an ionic impurity contained in a polymer (F) to a polymer (F), After an ionic impurity contained in a polymer (F) by removing this salt from a polymer (F) shall be 50 ppm or less, a hydrolytic silicon group is introduced into a polymer (F), and it is considered as an organic polymer (A).

[0047]An ionic impurity contained in a terminal unsaturated group introduction thing (G) of a polymer (F), After an ionic impurity contained in a terminal unsaturated group introduction thing (G) by removing this salt from a terminal unsaturated group introduction thing (G) after considering it in a terminal unsaturated group introduction thing (G) as an insoluble salt intrinsically shall be 50 ppm or less, it is made to react to a silicon hydride compound expressed with a terminal unsaturated group introduction thing (G) and a formula (2), and is considered as an organic polymer (A).

[0048]A molecular weight of an organic polymer (A) in this invention is computed based on a hydroxyl value conversion value molecular weight of a polymer (F) which is a raw material. As for this molecular weight, 5000-30000 are preferred. If elongation will become hard low in a cured body if lower than 5000, and 30000 is exceeded, pliability and elongation of a cured body are satisfactory, but viscosity of the polymer itself [this] becomes remarkably high, and practicality becomes low.

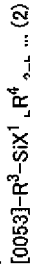
Especially 8000-30000 are preferred.

[0049][in catalyst] A curing catalyst (B) and an organic amine compound (C) which are chosen from carboxylate of divalent tin, carboxylate of divalent bismuth, and carboxylate of divalent lead in this invention are used. Although these metal carboxylate itself acts to promote hardening of an organic polymer (A), it is insufficient for the purpose of this invention, and it is indispensable to use together with an organic amine compound (C).

[0050]As for a curing catalyst (B), it is preferred that it is a salt of with a carbon number of 20 or less of straight chain shape or a letter of branching aliphatic carboxylic acid. As with a carbon number of 20 or less aliphatic carboxylic acid, there are heptanoic acid, octylic acid, decanoic acid, lauric acid, stearic acid, etc. A curing catalyst (B) may be a mixture.

[0051]Especially the amount of these metal carboxylate used has 0.01 - 3 preferred weight section 0.01 to 10 weight section to organic polymer (A) 100 weight section.

[0052]As an organic amine compound (C) of this invention, with a carbon number of 20 or less monoamine or with a carbon number of 20 or less polyamine is preferred. A compound which has a hydrolytic silicon group expressed with an amino group and a formula (2) to intramolecular is preferred.



[0054]As for a divalent organic group and R⁴, a hydroxyl group or a hydrolytic basis, and b of substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and X¹ are [R³] the integers of 1-3 among a formula.

[0055]As with a carbon number of 20 or less amine, it is preferred to be chosen out of with a carbon number of 20 or less aliphatic series mono(or poly) amine, with a carbon number of 20 or less alicyclic felloows mono(or poly) amine, and with a carbon number of 20 or less aromatic mono(or poly) amine for example. Specifically, the following can be illustrated.

[0056]Monoamine : Methylamine, ethylamine, propylamine, isopropylamine, A butylamine, amyl amine, hexylamine, octylamine, nonyl amine, Lauryl amine, dimethylamine, diethylamine, dipropyl amine, diisopropylamine, dibutyl amine, diamylamine, trimethylamine, Triethylamine, tripropylamine, tributylamine, triamylamine, Cyclo propylamine, a cyclo butylamine, cyclopentyl amine, cyclohexylamine, aniline, N-methylaniline, NN-dimethylaniline, N-ethylaniline, NN-diethylaniline, a toluidine, benzylamine, diphenylamine, etc.

[0057]Polyamine : Ethylenediamine, diethylenediamine, triethylenediamine, Hexamethylenediamine, dodecamethylenediamine, diethylenetriamine, Triethylenetetramine, tetraethylenepentamine, diethanolamine, triethanolamine, N,N,N'-tetramethyl 1,3-butanediamine, N,N,N' N'-tetramethylethylenediamine, etc.

[0058]As a compound which has a hydrolytic silicon group expressed with an amino group and a formula (2) to intramolecular, Especially a reactant with an organic amine compound which has a hydrolytic silicon group in intramolecular known as amino group content Silang, and a compound which has an epoxy group and a hydrolytic silicon group in intramolecular known as amino group content Silang and epoxy group content Silang is preferred.

[0059]As amino group content Silang, specifically gamma-aminopropyl trimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyl triethoxysilane, There are gamma-aminopropyl methyl dimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyl diethoxysilane, and N-(beta-aminoethyl)-gamma-aminopropyl methyl diethoxysilane.

[0060]As epoxy group content Silang made to react to these amino group content Silang, gamma-glycidyloxypropyl trimethoxysilane, There are gamma-glycidyloxy propyl triethoxysilane, gamma-glycidyloxy propylmethyl dimethoxysilane, gamma-glycidyloxy propylmethyl diethoxysilane, etc. [0061]receiving organic polymer (A) 100 weight section in an organic amine compound (C) in this invention -- 0.01 -- **** for 10 weight sections -- things are preferred. 0. Especially one to 3 weight section is preferred.

[0062]A bulking agent (D) is used in this invention. As for especially the amount of bulking agent used, 50 to 250 % of the weight is preferred zero to 1000% of the weight to an organic polymer (A). The following are mentioned as an example of a bulking agent. These bulking agents may be used independently and may be used together two or more sorts.

[0063]An example of a bulking agent : Calcium carbonate, fumes silica, sedimentation nature silica, a silicic acid anhydride, Hydrous silicic acids and carbon black, magnesium carbonate, diatomite, Calcination clay, clay, talc, titanium oxide, bentonite, organic bentonite, Ferric oxide, a zinc oxide, an active white, a milk balloon, wood flour, pulp, a cotton chip, mica, and blacking wash farina -- rubbing -- fibrous fillers, such as powder state bulking agents, such as farina, graphite, aluminum impalpable powder, and the Flint powder, asbestos, glass fiber, a glass filament, carbon fiber, the Kevlar textiles, and a polyethylene fiber.

[0064]In this invention, a plasticizer can be used arbitrarily. As a plasticizer, dioctyl phthalate, dibutyl phthalate, phthalic acid diisononyl ester, Phthalic ester, such as phthalic acid benzyl butyl ester; Dioctyl adipate. Alcohol ester, such as aliphatic-carboxylic-acid ester; pentaerythritol ester, such as succinic acid diisodecyl, dibutyl sebacate, and butyl oleate; Trioctyl phosphate, Phosphoric ester,

such as tricresyl phosphate; epoxy plasticizer; chlorinated paraffins, such as epoxidized soybean oil, 4,5-epoxy hexahydrophthalic acid diethyl, and epoxy stearic acid benzyl, can be independent, or can use it with two or more sorts of mixtures.

[0065]The constituent of this invention can contain still more publicly known various additive agents etc. As an additive agent, thixotropy grant agents, such as adhesive grant agents, such as phenol resin and an epoxy resin, and hydrogenation castor oil, paints, various kinds of antiaging agents, an ultraviolet ray absorbent, etc. can be used.

[0066]

[Example]Although working example (Examples 1-6, 15-20, 29-34) and a comparative example (Examples 7-14, 21-28, 35-45) explain this invention concretely below, this invention is not limited to these. The synthetic examples 1-7 first show the example of manufacture of the organic polymers P1-P7 which are the raw materials of an organic polymer (A) (however, P7 organic polymer for comparison). A part shows a weight section.

[0067][Synthetic example 1] Propylene oxide is polymerized with a zinc hexa cyanocobaltate glyme complex by using the glycerin propylene oxide addition of the molecular weight 1000 as an initiator, Polyoxypolyene triol of hydroxyl value 11.2 mgKOH/g and viscosity 7000cP in 25 ** was obtained. Then, after adding the sodium methoxide of the equivalent 1.1 times to the hydroxyl group of polyoxypolyene triol, methanol was distilled off, and the organic polymer (P1) which added the allyl chloride, changed terminal hydroxyl groups into the allyloxy group, and contained metal salt as an impurity was obtained.

[0068][Synthetic example 2] Propylene oxide was polymerized with the zinc hexa cyanocobaltate glyme complex by having used ethylene glycol as the initiator, and the viscosity in hydroxyl value 9.3 mgKOH/g and 25 ** obtained polyoxypolyene diol of 8000cP. The organic polymer (P2) which changed terminal hydroxyl groups into the allyloxy group by the method of the synthetic example 1 description, and contained metal salt as an impurity was obtained.

[0069][Synthetic example 3] Propylene oxide was polymerized with the zinc hexa cyanocobaltate glyme complex by having used ethylene glycol as the initiator, and the viscosity in hydroxyl value 5.6 mgKOH/g and 25 ** obtained polyoxypolyene diol of 17000cP. Then, the organic polymer (P3) which changed terminal hydroxyl groups into the allyloxy group by the method of the synthetic example 1 description, and contained metal salt as an impurity was obtained.

[0070][Synthetic example 4] Propylene oxide is polymerized with a zinc hexa cyanocobaltate glyme complex by using the pentaerythritol propylene oxide addition of the molecular weight 1000 as an initiator. The viscosity in hydroxyl value 13.2 mgKOH/g and 25 ** obtained polyoxypolyene tetraol of 6000cP. The organic polymer (P4) which changed terminal hydroxyl groups into the allyloxy group by the method of the synthetic example 1 description, and contained metal salt as an impurity was obtained.

[0071][Synthetic example 5] After mixing the polyoxypolyene diol obtained in the synthetic example 3, and the polyoxypolyene triol obtained in the synthetic example 1 by the weight ratio 2 to 1, the organic polymer (P5) which changed terminal hydroxyl groups into the allyloxy group by the method of the synthetic example 1 description, and contained metal salt as an impurity was obtained.

[0072][Synthetic example 6] After mixing the polyoxypolyene diol obtained in the synthetic example 3, and the polyoxypolyene tetraol obtained in the synthetic example 4 by the weight ratio 4 to 1, the organic polymer (P6) which changed terminal hydroxyl groups into the allyloxy group by the method of the synthetic example 1 description, and contained metal salt as an impurity was obtained.

[0073][Synthetic example 7] In accordance with a method given in JP-59-25808.B, 4 mol of polyoxypolyene diol of the hydroxyl value conversion molecular weight 3000 is received. After making 3-mol chlorobromomethane react under alkali existence, the organic polymer (P7) which added the allyl chloride, changed terminal hydroxyl groups into the allyloxy group, and contained metal salt was obtained.

[0074][Examples 1-14] The organic polymers P1-P7 were refined by purification method A - I, and the amount of residual metal ions (unit: ppm) was measured. The viscosity (unit: cP) of the organic polymers P1-P7 after refining is also collectively shown in Tables 1-2.

[0075]Then, by the publicly known method using a platinum catalyst, the methyl dimethoxy silyl propyl group was introduced into the organic polymer terminal, and the organic polymers S1-S14 were

obtained. The after-manufacture viscosity of the organic polymers S1-S14 is also shown in a table. The content of the methyl dimethoxy silyl propyl group as an end group is the range of organic polymer 1g per 0.11mmol - 0.17mmol. The amount of residual metal ions of the obtained organic polymers S1-S14 was not different from before methyl dimethoxy silyl propyl group introduction. [0076][Examples 15-28] 160 copies of calcium carbonate, 60 copies of dioctyl phthalate, five copies of hydrogenation castor oil, one copy of phenolic antioxidant, 0.5 copy of ultraviolet ray absorbent, and 0.5 copy of light stabilizer were added and kneaded to 100 copies of organic polymers (S1-S14), and it was considered as base resin (M1-M14).

[0077]On the other hand, to ten copies of metal carboxylate shown in the Table 8 right column, three copies of lauryl amine, 20 copies of dioctyl phthalate, and 60 copies of calcium carbonate were kneaded, and it was considered as the hardening agent (K1-K5).

[0078]The viscosity (after-storage viscosity) (unit: cP) after storing for 14 days at the viscosity (after-manufacture viscosity) (unit: cP) immediately after manufacture of base resin and 50 ** was measured. A result is shown in Tables 3-4.

[0079][Examples 29-45] 100 copies of base resin (M1-M14) and 8.5 copies of hardening agents (K1-K5) which were shown in the table below were kneaded, the hardenability constituent was slushed so that it might become a thickness of 3 cm into the cup of a cylindrical shape 4 cm in diameter, and it was neglected under the atmosphere of 20 ** and 65% humidity for 8 hours. The situation of hardening to a depth direction from the surface was seen using the penetrator based on JISK-2530 after that. A result is shown in Tables 5-7. The one where penetration is larger means that hardening from the surface is not progressing.

[0080][Purification method A] The polyoxypropylene polymer 5g, the water 50g, and the disodium dihydrogen pyrophosphate 10g of the molecular weight 10000 to which 10 % of the weight of ends were made to carry out block polymerization of the ethylene oxide were added to 1 kg of organic polymers which contain metal salt etc. as an impurity, and it agitated at 90 ** for 1 hour. Then, after distilling off water under 90 ** and decompression, after adding 10 g and carrying out decompression drying of the KYO word 600 (synthetic MAGUNE SIMM silicate, harmony chemicals company make) at 90 ** for 1 hour, 2 l. of hexane was added, the organic polymer was dissolved, and the insoluble matter was filtered and removed using the filter paper. It distilled off under decompression of hexane after that, and refining things were obtained.

[0081][Purification method I] 1 kg of organic polymers which contain metal salt etc. as an impurity were dissolved in 3 kg of hexane, 1 kg of sulfuric acid water was added 3% of the weight, and the whole has become turbid although agitated for 1 hour. Although allowed to stand at the room temperature for three days, since the whole hexane layer a little transparent [about 1/5] to the top layer dissociated, the hexane layer was divided by the decantation, hexane was distilled off under decompression, and refining things were obtained.

[0082]

[Table 1]

例	1	2	3	4	5	6	7
原料重合体	P1	P2	P3	P4	P5	P6	P7
精製法	ア	ア	ア	ア	ア	ア	ア
精製後粘度	6500	7500	15000	5500	12000	13000	9000
残存イオン量							
Na ⁺ 量	3	4	2	5	3	3	2
Zn ²⁺ 量	1以下	1以下	1以下	1以下	1以下	1以下	1以下
Cu ²⁺ 量	1以下	1以下	1以下	1以下	1以下	1以下	1以下
Cl ⁻ 量	5	5	3	8	5	5	5
有機重合体	S1	S2	S3	S4	S5	S6	S7
製造後粘度	8000	9000	17000	7500	13000	13500	9500

[0083]

[Table 2]

例		8	9	10	11	12	13	14
原料重合体	P1	P2	P3	P4	P5	P6	P7	
精製法	イ	イ	イ	イ	イ	イ	イ	
精製後粘度	6500	7500	15000	5500	12000	13000	9000	
残存イオン量								
Na ⁺ 量	25	22	32	35	26	38	2	
Zn ²⁺ 量	5	3	3	5	4	5	0	
Cu ²⁺ 量	2	4	3	3	4	5	0	
Cl ⁻ 量	35	36	40	45	35	44	4	
有機重合体	S8	S9	S10	S11	S12	S13	S14	
製造後粘度	9000	10000	19000	8500	13000	16000	9500	

[0084]

[Table 3]

例		15	16	17	18	19	20	21
有機重合体	S1	S2	S3	S4	S5	S6	S8	
主剤	M1	M2	M3	M4	M5	M6	M7	
製造後粘度	15万	16万	24万	13万	17万	20万	17万	
貯蔵後粘度	16万	16万	25万	13万	18万	21万	35万	

[0085]

[Table 4]

例		22	23	24	25	26	27	28
有機重合体	S9	S10	S11	S12	S13	S7	S14	
主剤	M8	M9	M10	M11	M12	M13	M14	
製造後粘度	18万	26万	15万	19万	20万	17万	17万	
貯蔵後粘度	45万	55万	37万	40万	52万	18万	18万	

[0086]

[Table 5]

例		29	30	31	32	33	34
主剤	M1	M2	M3	M4	M5	M6	
硬化剤	K1	K1	K1	K2	K3	K4	
針入度	0.7	0.7	0.5	0.8	0.7	0.5	

[0087]

[Table 6]

例	35	36	37	38	39	40
主 剤	M7	M8	M9	M10	M11	M12
硬化剤	K1	K1	K1	K2	K3	K4
針入度	0.6	0.6	0.4	0.7	0.5	0.4

[0088]

[Table 7]

例	41	42	43	44	45
主 剤	M7	M14	M1	M2	M3
硬化剤	K1	K1	K5	K5	K5
針入度	1.5	1.5	2.5	2.5	2.1

[0089]

[Table 8]

硬化剤	含有する金属カルボン酸塩
K 1	オクチル酸スズ (2価) (日本化学産業製ニッカオクチックスズ)
K 2	オクチル酸ビスマス (2価) (長瀬化成社コスキャット 83)
K 3	パーサチタック酸ビスマス (2価) (The Shepherd Chemical 社 SHEPHERD VERSHATE)
K 4	ネオデカノン酸ビスマス (2価) (The Shepherd Chemical 社 NEODECANOATE)
K 5	ジブチルスズジラウレート (4価)

[0090]

[Effect of the Invention] Storage stability is improved remarkably and the hardenability constituent of this invention has the good hardenability of the depths.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by regulation of Patent Law Article 17 of 2

[Section Type] The 3rd Type of the part III gate

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[Written Amendment]

[Filing date] Heisei 11(1999) March 10

[Amendment 1]

[Document to be Amended] Description

[Item(s) to be Amended] Claims

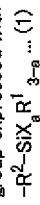
[Method of Amendment] Change

[Proposed Amendment]

[Claim(s)]

[Claim 1] A curing catalyst (B) chosen from the following organic polymer (A), carboxylate of divalent tin, carboxylate of divalent bismuth, and carboxylate of divalent lead, and an organic amine compound (C) and a room-temperature-curing nature constituent containing a bulking agent (D).

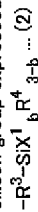
(Organic polymer) It is derived from a hydroxyl group content polyoxyalkylene polymer (F) produced by polymerizing alkylene oxide in an initiator by making a composite metal cyanide complex (E) into a catalyst. An organic polymer (A) whose total amount of an ionic impurity it has a hydrolytic silicon group expressed with a formula (1), and is 50 ppm or less.



As for R¹, a hydroxyl group or a hydrolytic basis, and a of substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and R² are the integers of 1-3 a divalent organic group

and X among a formula.

[Claim 2] The room-temperature-curing nature constituent according to claim 1 whose organic amine compound (C) is a compound which has with a carbon number of 20 or less amine or a hydrolytic silicon group expressed with an amino group and a formula (2) to intramolecular.

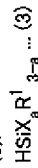


As for a divalent organic group and R⁴, a hydroxyl group or a hydrolytic basis, and b of substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and X¹ are [R²] the integers of 1-3 among a formula.

[Claim 3] The room-temperature-curing nature constituent according to claim 1 or 2 which is an ionic impurity in which an ionic impurity contains metallic compounds and/or an alkali metal compound resulting from a composite metal cyanide complex (E).

[Claim 4] An organic polymer (A) an ionic impurity contained in a polymer (F). After an ionic impurity contained in a polymer (F) by removing this salt from a polymer (F) after considering it to a polymer (F) as an insoluble salt intrinsically shall be 50 ppm or less. The room-temperature-curing nature constituent according to any one of claims 1 to 3 which is an organic polymer produced by introducing a hydrolytic silicon group into a polymer (F).

[Claim 5] An organic polymer (A) an ionic impurity contained in a terminal unsaturated group introduction thing (G) of a polymer (F). After an ionic impurity contained in a terminal unsaturated group introduction thing (G) by removing this salt from a terminal unsaturated group introduction thing (G) after considering it in a terminal unsaturated group introduction thing (G) as an insoluble salt intrinsically shall be 50 ppm or less. The room-temperature-curing nature constituent according to any one of claims 1 to 3 which is an organic polymer obtained by making it react to a silicon hydride compound expressed with a terminal unsaturated group introduction thing (G) and a formula (3).



A hydroxyl group or a hydrolytic basis, and a of R¹ are the integers of 1-3 among a formula substitution of the carbon numbers 1-20 or an unsubstituted univalent hydrocarbon group, and X.
[Claim 6] The room-temperature-curing nature constituent according to any one of claims 1 to 5 whose hydroxyl value conversion molecular weights of a polymer (F) are 5000-30000.

[Translation done.]